

Modification of Zeolite Catalyst with SiO₂ from Fly Ash for Palm Oil Hydrocracking Process

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Abstract

Zeolite is an alumina-silica crystal that has two types of acid sites in the framework, namely Bronstead acid sites and Lewis acids. Natural zeolite has many benefits, one of which is as a catalyst for the cracking process. This research aims to determine the characteristics of zeolite catalysts modified by inserting Si and the effect of variations in Si insertion in the zeolite catalyst on the activity and selectivity of the catalyst in the hydrocracking process of MEPO to become biogasoline. This research began with the preparation of natural zeolite, activation of the zeolite by adding HF, HCl and NH₄Cl solutions, then continued with the hydrothermal process until the H5NZA catalyst was obtained. The H5NZA catalyst was inserted with 1%, 2%, 3% and 4% Si originating from fly ash. Catalyst characteristics include the Si/Al ratio content and acidity. The hydrocracking process was carried out in a flow fixed bed system reactor column with a temperature of 450oC and a hydrogen gas flow rate of 20 mL/minute. The catalyst used in hydrocracking is 3 grams. The hydrocracking results were analyzed using GC-MS so that the activity and selectivity of the H5NZASi catalyst could be determined. The research results showed that the modified zeolite had an increase in the Si/Al ratio and acidity. The H5NZASi catalyst with a variation of 2% has the highest ratio, namely 5.5499. Meanwhile, the highest catalyst acidity was the 3% variation of the H5NZASi catalyst, namely 1.2337 mmol/gram. The relationship between catalyst characteristics such as Si/Al ratio and acidity increases with increasing Si inserted. Si insertion increases the ability of the catalyst in MEPO hydrocracking to produce a liquid product with an activity of 73.4% and selectivity for biogasoline fractions of 45.37% using a 3% H5NZASi catalyst.

Keywords : MEPO, zeolit, Hidrorengkah, biogasoline.

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I. INTRODUCTION

Zeolites have two types of acid sites in the framework, namely Bronstead acid sites in the form of protons attached to an oxygen framework bonded to silicon atoms around the aluminum atom and Lewis acids which are formed from the dehydroxylation of two adjacent Bronstead acid groups (Oudejans, 1984), site This acid plays a role in catalytic cracking. Natural zeolite is a natural mineral with the main composition of around 70% mordenite. Natural zeolite needs to be activated and modified to improve its characteristics, including the Si/Al ratio and catalytic activity. Natural zeolite is mixed with many impurities other than zeolite, both crystalline and amorphous. Increasing the Si/Al ratio can be done by inserting Si metal into the zeolite catalyst. According to Handoko (2013), the insertion of Si metal from sodium silicate in the zeolite catalyst resulted in an increase in the Si/Al ratio of 40.17%.

Research on hydrocracking palm oil into biogasoline using a zeolite catalyst modified with SiO₂ from fly ash. The SiO₂ extraction process was carried out using 3M NaOH, then precipitated using 1M HCl (Retnosari, 2013). The next step, sodium silicate is made by reacting the obtained silica and NaOH solution with a weight ratio of 2:3 (Adziimaa et al, 2013). Palm oil is transesterified first into palm oil methyl ester and converted into biogasoline through a hydrocracking process. The hydrocracking process was carried out in a flow fixed bed system reactor column with a temperature of 400oC and a hydrogen gas flow rate of 20 mL/minute. The catalyst used in this research is the H5NZASi catalyst which is made by dissolving the H5NZA catalyst into sodium silicate, with variations of Si metal of 0%, 1%, 2%, 3% and 4% by weight of the catalyst. The product obtained from hydrocracking will be analyzed using GC-MS.

II. RESEARCH METHODS

Equipment

The equipment used in the research were 50, 100, and 250 ml beakers, 50 ml measuring cups, 100 and 250 ml measuring flasks, 100 ml three-neck flasks, Erlenmeyer, dropper pipettes, 10 and 25 ml volume pipettes, magnetic stirrer, furnace, 100 mesh sieve, oven, analytical balance, thermometer, atomic absorption spectrophotometer (AAS), Gas Chromatography-Mass Spectroscopy (GC-MS), a set of flow fixed bed reactor, desiccator, porcelain cup, separating funnel, and pH meter.

Material

The materials used in the research were natural zeolite, fly ash from PLTU Paiton-Probolinggo, Methyl ester palm oil (lemigas), NH₄Cl 99.8% (merck), HF 49% (merck), HCl 37% (merck), KOH p.a., NaOH (merck), Whatman 41 filter paper, methanol p.a., NH₃ 25% p.a., distilled water (technical), hydrogen gas (samator), oxygen gas (samator), and nitrogen gas (samator).

Procedure

a. SiO₂ Extraction from Fly Ash

A 50 gram sample (fly ash) originating from the Paiton-Probolinggo PLTU was taken and soaked in hot water for 2 hours. Decanted then dried at 100 for 24 hours. The prepared samples were refluxed with 5 M HCl solution for 5 hours, filtered and dried in an oven at 100 °C. A total of 25 grams of sample was soaked in 150 ml NaOH solution with a concentration of 3 M and heated at a temperature of 65-70°C accompanied by stirring at a speed of 150 rpm for 3 hours. The sample is filtered and the filtrate is collected. The 1 M HCl solution was added to the filtrate gradually until the formation of precipitate stopped (pH 7). The precipitate was separated and washed with hot distilled water to remove excess acid. The precipitate obtained from this treatment was then dried in an oven at 80 for 6 hours to remove water.

b. Natural Zeolite Preparation

Soak the natural zeolite in distilled water while stirring for 24 hours. Filtered and dried in the oven at 120 for 12 hours. Zeolite is named NZ catalyst.

c. Zeolite Activation

The prepared zeolite was soaked with 2% HF for 30 minutes and washed again with distilled water 3 times. Oven at 120 °C for 3 hours and cool. Next, acidification was carried out by washing with 2 M HCl with a ratio of zeolite:HCl = 1:2 (v/v) while stirring for 20 to 30 minutes, then washed with distilled water until pH=6 and dried using an oven at 120°C for 3 hours. The zeolite was cooled again and added with a 2 M NH₄Cl solution with a ratio of 1:2 (v/v) in a glass beaker and heated at a temperature of 90°C for 4 hours with a magnetic stirrer (Zhang, 1999). The zeolite obtained was used as a catalyst and was named NZA catalyst (active zeolite).

d. Preparation of NZASi Catalyst

The NZA catalyst was refluxed using silica which had been dissolved in distilled water at a temperature of 750°C for 2 hours. Then the mixture was dried at a temperature of 120°C for 2 hours to obtain the NZASi catalyst (Yuanita, 2009). The Si levels contained in sodium silicate are 0%, 1%, 2%, 3% and 4%.

e. Catalytic Calcination, Oxidation and Reduction Process

The NZASi catalyst is inserted into the reactor to be calcined using N₂ gas, oxidized with O₂ gas and finally reduced with H₂ gas. Gas flow was carried out with Zeolite which had been supplied with gas at a gas flow rate of 20 ml/minute for 3 hours at a temperature of 500°C (Handoko, 2013). The catalyst was named H5NZASi. The prepared zeolite, NZA catalyst, and H5NZASi catalyst obtained were analyzed to determine their characteristics including the Si/Al ratio using AAS and total acidity gravimetrically.

f. Hydrocracking of MEPO with H5NZASi Catalyst

10 grams of MEPO was placed in a feed tank equipped with a heater and 3 grams of H5NZASi catalyst was placed in a flow fixed bed type reactor column. The reactor column is heated to a temperature of 450°C and the feed tank is heated to evaporate the MEPO. H₂ gas as the feed carrier gas is flowed at a gas flow rate of 20 mL/minute and carries the feed to the catalytic reactor column. The reaction product in the form of gas is passed into a condenser (cooler) until it turns into liquid and is stored in a container. The MEPO hydrocracking process is carried out for 30-60 minutes. The products obtained were analyzed using GC-MS.

g. Catalyst Activity and Selectivity

Catalytic activity towards the product is defined as the amount of hydrocracking product compared to the amount of MEPO before hydrocracking.

$$\text{Aktivitas}(\%) = \frac{\text{Jumlah produk hasil perengkahan}}{\text{jumlah MEPO sebelum perengkahan}} \times 100\% \quad (1)$$

Catalyst selectivity is the ability of a catalyst to support one or several types of desired products, namely the short fraction (gasoline) C5-C11 and the medium fraction (kerosene) C12-C18 from all possible product types compared to the initial concentration of the reactants.

"Selectivity" ("%") = Amount of hydrocarbon compound product"

III. RESULTS AND DISCUSSION

a. Catalyst Characterization Results

The initial process carried out is washing the zeolite so that it is free from impurities found inside and outside the zeolite surface. then modified by being given several treatments such as dealumination, calcination, oxidation, hydrothermal and Si insertion processes. The modified zeolite was measured for its Si/Al ratio and acidity. The Si/Al ratio is one of the characteristics of zeolites that is important to know, because the Si and Al content can influence the properties of the zeolite as a catalyst. The analysis results show that the Si/Al ratio of natural zeolite in this study was 3.9619. The Si/Al ratio value of zeolite is relatively small, this can happen because the amount of Al in the natural zeolite framework is greater than the amount of Si. Zeolite with a high Si/Al ratio value will also tend to be hydrophobic and react more easily with organic compounds or hydrocarbons which are also non-toxic. polar (Gates, 1992). The results of analysis using atomic absorption spectroscopy of natural zeolites that have undergone activation and modification are presented in Figure 1.

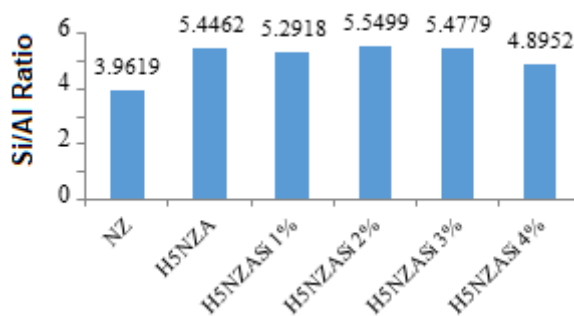


Figure 1. Si/Al ratio graph

The increase in the Si/Al ratio from the NZ to H5NZA catalyst is 5.4462. This increase in ratio occurs because the NZ catalyst reduces the amount of Al in the catalyst, so the value of the Si/Al ratio increases. The H5NZA to H5NZASi catalyst with several variations did not experience a large change in the Si/Al ratio value. This is possible because the addition of Si to the H5NZA catalyst is not in large quantities, and only a small difference, so that the Si that enters the zeolite framework does not have too big an impact. The 1%, 3%, and 4% H5NZASi catalysts experienced a decrease in the Si/Al ratio value. This is possible because Si does not enter the zeolite framework and does not spread evenly. The acidity of the catalyst was measured using a gravimetric method based on the difference in weight of the zeolite before and after adsorbing ammonia gas (NH_3). The acidity obtained is an accumulation of Bronsted acid sites and Lewis acid sites, both on the surface and in the pore cavity. The acidity of each catalyst is shown in figure 2.

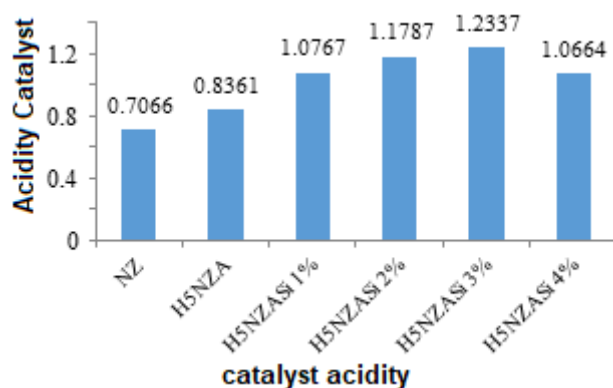


Figure 2. Acidity of each catalyst

The acidity of the Si-inserted catalyst increases with increasing concentration of the inserted Si. The greater the concentration of Si inserted into the zeolite will cause the higher the acidity of the zeolite. It can be understood that the metal cations dispersed in H5NZA have orbitals that are not yet fully filled with electrons, so they are very effective as electron pair acceptors from the adsorbate base.

b. Catalytic activity

Catalyst activity is based on the catalyst's ability to convert reactants into new liquid organic products from a number of reactants (weight/g). The amount of catalytic activity in percent shows the ability of the catalyst to produce new compounds. The total concentration of hydrocracking results is obtained from the GC chromatogram, the activity value here is the percentage of the total concentration of new compounds from catalytic cracking with tR other than the reactants divided by the total concentration of the initial reactants. The percentage of activity of each catalyst in the cracking process is shown in the figure

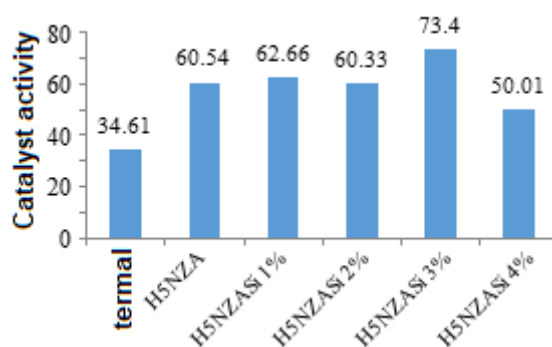


Figure 3. Catalyst activity for each catalyst

Figure 3 shows the highest activity of cracking results in breaking carbon chain bonds in the reactants, from methyl palmitate and palmitic acid compounds which have long carbon chains to compounds which have short carbon chains (C₅-C₁₁ and C₁₂-C₁₈) owned by the 3% H5NZASi catalyst if compared to the activity of other types of catalysts and thermal cracking, namely 73.4%. This shows that the addition of 3% Si in the H5NZA catalyst provides an increase in activity when compared to the activity of zeolites that do not use a catalyst (thermal), do not add Si, or those that add 1%, 2% and 4% Si. This phenomenon shows that the surface adsorption power of the 3% H5NZASi catalyst interacting with the reactants is much greater than other catalysts and thermal cracking. Insertion in a catalyst can increase adsorption power, this can be understood because metal orbitals are not yet completely filled with electrons, so their reactive nature makes it easier to adsorb reactants and release catalytic products.

But this does not apply to the addition of Si with a concentration of 4%. This may occur because Si accumulates in several zeolite pores and is not distributed evenly throughout the zeolite pore surface, thus causing fouling on the catalyst surface and reducing the catalyst surface area. As a result, the active side of the catalyst will decrease and its activity as a catalyst will also decrease. Therefore, the 4% H5NZASi catalyst has less activity compared to the H5NZA catalyst, because in the H5NZA catalyst there is no impurity on the catalyst surface.

c. Catalyst selectivity

Selectivity is the ability of a catalyst to direct it to a certain type of product. Product selectivity can be seen from the peak distribution of each cracking product obtained. All selectivity compounds produced in this study were grouped into 2 fractions, the first is the light fraction (biogasoline), namely compounds with C₅-C₁₁ hydrocarbon chains and the medium fraction (biokerosene), namely compounds with C₁₂-C₁₈ hydrocarbon chains.

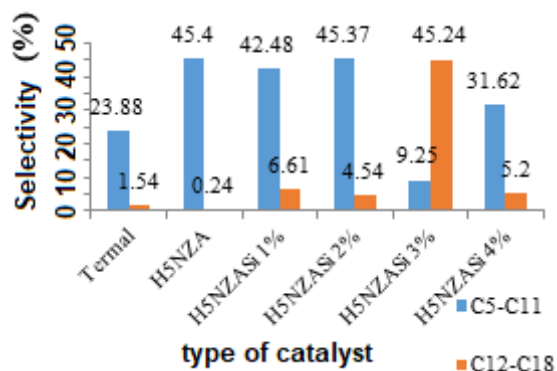


Figure 4. Catalyst Selectivity for each Catalyst Type

The catalyst selectivity process for each catalyst is dominated by products with short fraction hydrocarbons (C₅-C₁₁) except for hydrocracking using a 3% H5NZASi catalyst where the product produced is mostly medium fraction hydrocarbons (C₁₂-C₁₈).

d. Relationship between Si/Al Ratio and Catalyst Activity and Selectivity

The Si/Al ratio in the zeolite framework will determine the level of polarity of the zeolite as a catalyst. Zeolite with a low Si/Al ratio will have more polar properties compared to zeolite with a high Si/Al ratio. The reactant used (MEPO) is nonpolar so a catalyst with a high Si/Al ratio is needed. The graph in Figure 4 shows the relationship between the Si/Al ratio and catalyst activity.

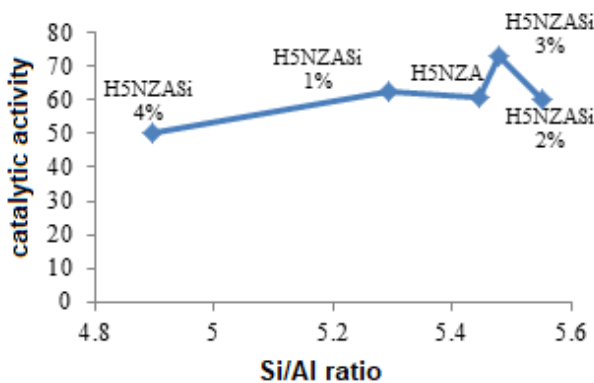


Figure 4 Relationship between catalyst activity and Si/Al ratio

The relationship between the Si/Al ratio and catalyst activity shows a trend that the higher the Si/Al ratio value, the higher the catalyst activity. The 2% and 3% H5NZASi catalysts experienced a decrease in activity values. This is likely caused by the uneven distribution of Si on the catalyst surface resulting in buildup on the catalyst surface which results in low activity values.

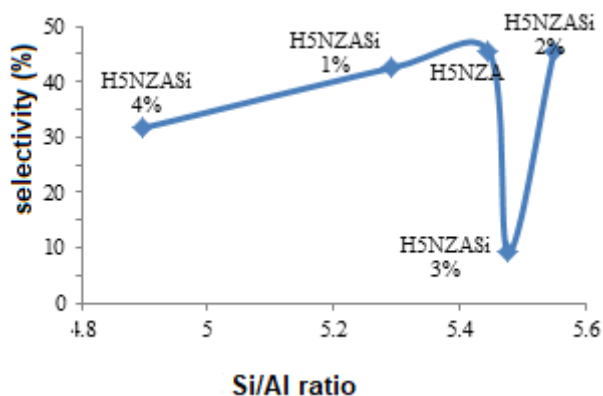


Figure 5. Relationship between Si/Al Ratio and Catalyst Selectivity

The relationship between the Si/Al ratio and catalyst selectivity in Figure 5 shows that the greater the Si/Al ratio, the greater the catalyst selectivity. If the Si/Al ratio decreases, selectivity also decreases. 2% H5NZASi catalyst with a Si/Al ratio of 5.5499 produces a selectivity of 45.37. A catalyst with a high Si/Al ratio will have high thermal stability (Hamdan, 1992) and be effective in cracking non-plastic compounds (Sutarti and Rahmawati, 1994). If a catalyst contains more silicon, the activity towards non-polar molecules will increase because the Si-O group is neutral. Silicate zeolite which is neutral will have minimal polarity so that it has a more favorable effect on the adsorption of non-polar reactants, namely non-polar compounds (Sutarti and Rahmawati, 1994). For the 3% H5NZASi catalyst, the selectivity value of the catalyst towards the biogasoline fraction is small. This is because with the 3% H5NZASi catalyst the product produced is mostly medium fraction hydrocarbon compounds.

e. Relationship between Acidity and Catalyst Activity and Selectivity

The ability of the catalyst to adsorb NH₃ indicates the total acidity value. The acidity of the catalyst is strongly influenced by the acid site of the catalyst. According to Satterfield (1980), the acidity of a catalyst is defined as the ability of the catalyst to adsorb ammonia base due to the presence of Bronsted acid sites and Lewis acid sites on the catalyst surface. The more acid sites on the catalyst allow more NH₃ to be absorbed. The results of catalyst activity are influenced by the acidity value, when connected it will produce the graph below.

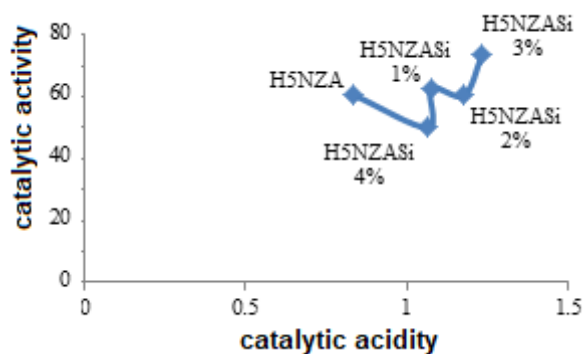


Figure 6. Relationship between acidity and catalyst activity

Based on the picture above, the 3% H5NZASi catalyst has the highest acidity compared to other catalysts, was 1.2337 mmol/gram. High acidity will have an impact on the number of carbonium ions formed, which will cause more collisions to occur with reactants which can affect the amount of product produced during the cracking process.

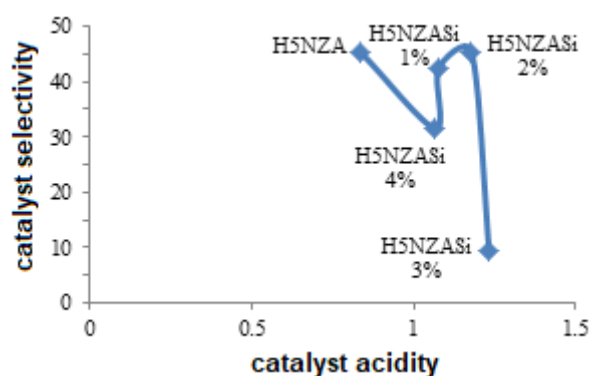


Figure 7. Relationship between Acidity and Catalyst Selectivity

The relationship between acidity and selectivity for the biogasoline fraction in Figure 4.16 shows that the greater the acidity of the catalyst, the greater the selectivity for the biogasoline fraction. Catalysts with high acidity have more acid sites. These many acid sites will later influence the catalytic hydrocracking process. However, for some 1% H5NZASi and 3% H5NZASi catalysts, the selectivity value for the bio gasoline fraction decreased. This is because the results of hydrocracking on the 1% and 3% catalyst variations tend to be in the medium fraction (C12-C18).

IV. CONCLUSIONS AND RECOMMENDATIONS

The conclusion that can be obtained from and discussing this research is that the Si/Al ratio is the highest on the 2% H5NZASi catalyst, amounting to 5.5499% and the highest acidity is found on the 3% H5NZASi catalyst, was 1.2337 mmol/g. The activity of the 3% H5NZASi catalyst was 73.40% and the selectivity was 45.37% on the 2% H5NZASi catalyst. The highest catalyst activity was H5NZASi

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